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Ceramic fillers in Li-Ion Battery Electrolytes

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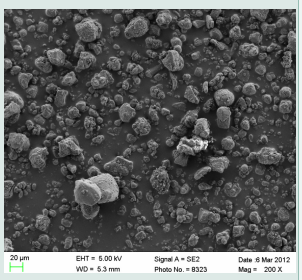
Summary

- Only partial dispersion stability of fillers in liquid electrolytes
- Very good dispersion stability in polymer gel electrolytes
- Particle containing gel electrolytes with optimal electrochemical properties and processability



Motivation

- **Utilization of particles as additional lithium source**
- **Enabling of additional Li-transport mechanisms**
- **Enhancing of Li diffusion constants**
- **Saving of expensive electrolytes**

Strategy

appropriate electrolyte systems → suitable ceramic filler → chemical stability of the filler in the matrix system → possible dispersants, if needed → electrochemical characterization → identification of conducting mechanisms

Properties of filler materials and dispersants

Selection of fillers:

- Availability and toxicity
- Beneficial effects
- Processability
- Lithium content
- Particle surface and particle size
- Price

Selection of dispersants:

- Availability and toxicity
- Processability
- Solubility in battery electrolytes/solvents
- Surface chemistry
- Electrochemical stability
- Price

Filler	Specific surface (measured) $m^2\ g^{-1}$	Particle size (manufacturer) [µm]	Particle size (measured) [µm]
Aluminiumoxid (Al_2O_3)	134,8	0,05	2,9 ± 1,1
Zirkoniumdioxid (ZrO_2)	9,0	0,03	7,8 ± 2,9
Bariumtitanat ($BaTiO_3$)	9,3	0,1	0,15 ± 0,22 10,1 ± 11,8
Lithiumorthosilikat (Li_4SiO_4)	3,1	149	11,5 ± 7,9
Lithiumaluminiumoxid ($LiAlO_2$)	9,6	110	35,1 ± 18,5

Stabilization of fillers

Electrostatic stabilization | Steric stabilization | Electrosteric stabilization

- Long-term stabilization in liquid electrolytes difficult
- Ligand exchange reactions on the surface of particles possible

Stabilization in liquid electrolytes

- System: Dispersant + ceramic filler + propylene carbonate
- Aim: Long-term stability in electrolyte solvents
- Proof: Visual observation and UV-Vis measurement

Dispersant	Al_2O_3	$LiAlO_2$	Li_4SiO_4	$BaTiO_3$	ZrO_2
Glycanate	++	-	- -	+	- -
Polyvinylpyrrolidon K17 (PVP K17)	+++	-	- -	+	- -
Polyethylenglykol (n=200)	++	-	- -	+	- -
Polyethylenglykolethylether-methacrylate (n=246)	++	-	- -	+	- -
Triethylcitrate	++	-	- -	+	- -
Acetyltributylcitrate	++	-	- -	+	- -

→ Strong relationship between particle size and dispersion stability

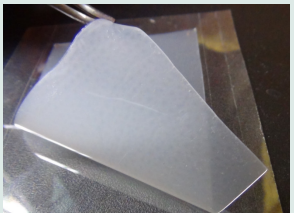
→ Only moderate stability is obtained

+++ no sedimentation for at least 60 h
++ sedimentation after 48 h
+ sedimentation after 12 h
- sedimentation after 30 min
-- sedimentation after 5 min

Stabilization in gel polymer electrolytes

- Stabilization in gel polymer electrolytes is obtained by using appropriate gel polymer matrices (PVdF-HFP and polymethylmethacrylate)
- A filler content up to several % inorganic particles can be reached
- Conducting salts: $LiPF_6$, lithium bis(trifluoromethanesulfonyl)azanide, $LiBF_4$

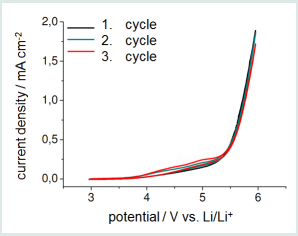
A gel polymer electrolyte based on PVdF-HFP (including liquids and conducting salts)



A gel polymer electrolyte based on PVdF-HFP with ceramic particles (Al_2O_3; including liquids and conducting salts)

Electrochemical Properties

- Water content has to be considered (< 20 ppm)
- Use of ionic liquids enables after-processing-drying
- Electrochemical stability up to 4 – 5 V vs. Li/Li+ (Pt vs. Li/Li)
- Specific conductivity: ~ 1 mS cm^{-1} in dependence of composition



Conclusions

- **In liquid electrolytes**, the preparation of particle-filled is challenging
- Very good processability of selected fillers in **gel polymer electrolyte** matrices (polymer, liquid phase, and conducting salt)
- **Particle size** is crucial for stabilization and processability
- Accurate **electrochemical properties** of particle-filled polymer electrolytes

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